
III.A.6 Novel Cathodes Prepared by Impregnation Procedures

Objectives

- Examine the feasibility of using different precursor species to impregnate lanthanum strontium manganite (LSM) into porous yttria-stabilized zirconia (YSZ) using fewer steps.
- Determine whether the addition of Co species could be used to enhance performance of LSM-based cathodes.
- Assess the stability of impregnated lanthanum strontium ferrite (LSF)-YSZ cathodes.
- Compare the fabrication cost of impregnated cathodes to one made by screen printing.

Accomplishments

- We showed that similar results were obtained when using various LSM precursors to produce LSM-YSZ cathodes.
- We showed that enhanced performance could be achieved by adding LSCo to LSM-YSZ cathodes.
- We have preliminary results showing that there is a slow deactivation with LSF-YSZ cathodes.

performance can be improved dramatically by replacing LSM with other perovskites, such as Sr-doped LaFeO_3 (LSF) or LaCoO_3 (LSCo) [1,2]. Unfortunately, it is not a simple matter to substitute these alternative perovskites for LSM. The conventional fabrication of LSM-YSZ composites involves a high-temperature calcination of LSM-YSZ mixtures to the electrolyte in order to establish good connectivity between the electrode and electrolyte. With LSM, calcination can be performed at 1,250°C, a temperature that is sufficiently high to sinter the YSZ in the electrode to the YSZ in the electrolyte, thus forming a good three-phase boundary. Unfortunately, it is not possible to calcine LSF-YSZ and LSCo-YSZ mixtures at high temperatures due to the fact that these oxides will undergo solid-state reactions.

An alternative approach to preparing composite cathodes involves eliminating high-temperature sintering of LSF (or LSCo) with YSZ. It has been pointed out that the driving force for reaction between the perovskites and YSZ disappears below 900°C. This implies that the problem of interfacial reactions may be primarily associated with processing the composite electrode, rather than fuel-cell operation, although interfacial reaction could also occur because of the reducing conditions associated with the electrode-electrolyte interface.

Introduction

While the performance of conventional Sr-doped LaMnO_3 (LSM)-YSZ cathodes is adequate at high temperatures, LSM-YSZ composites exhibit only modest performance at 700°C and poor performance at lower temperatures. Since there is a move towards operation at lower temperatures, cathodes with properties superior to LSM-YSZ are clearly needed. In fact, cathode

Approach

One way to form an oxide composite that is well connected to the electrolyte, while avoiding the high-temperature co-firing of YSZ and perovskite, involves adding the perovskite to a porous matrix of the YSZ that has already been sintered to high temperatures. The porous YSZ matrix can be produced by simple methods, such as tape casting or tape calendaring with pore formers. The tapes with pore formers can be laminated onto electrolyte tapes in the green state and co-fired together with the green anode. Finally, the perovskite is incorporated into the porous YSZ by infiltration.

Results

A. SOFC Cathodes Prepared by Infiltration with Various LSM Precursors

The cathode properties of LSM-YSZ composites formed by infiltration of porous YSZ with aqueous salt solutions, with LSM nano-particles, and with molten salts are essentially identical. The relatively high mobility of LSM on YSZ, associated with surface interactions between LSM and YSZ, causes the final composite structures to be essentially the same, independent of how the LSM is added. Figure 1 shows

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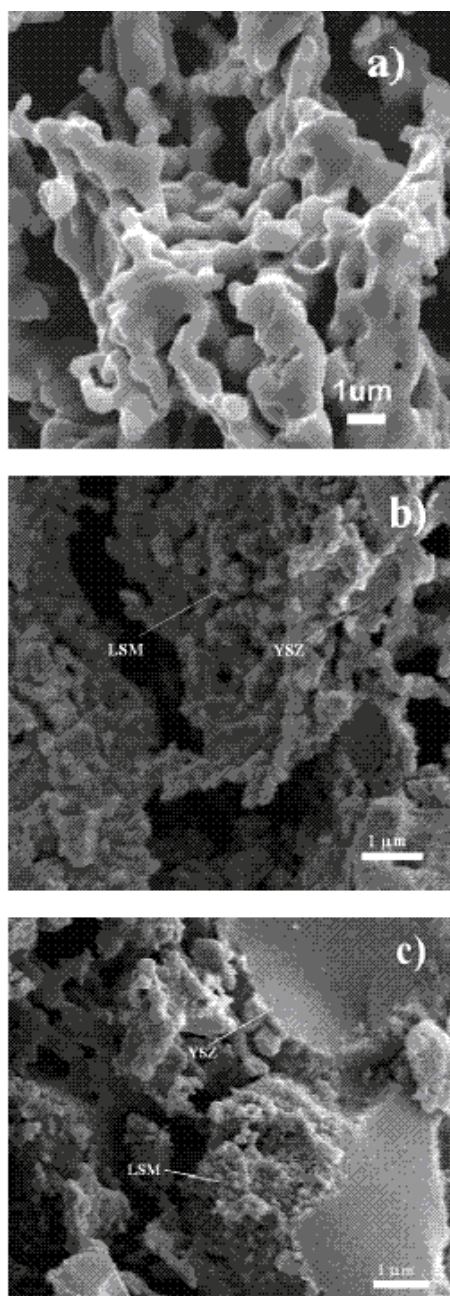


FIGURE 1. SEM images of a) the initial porous YSZ matrix; b) the LSM-YSZ composite prepared by infiltration of the LSM nano-particle suspension; c) the LSM-YSZ composite prepared by impregnation of LSM molten salts.

SEM images of a) the porous YSZ before impregnation, b) LSM-YSZ composite made by impregnation of LSM nano-particle suspension, and c) LSM-YSZ composite prepared by impregnation of the LSM molten salt. Figure 2 shows fuel cell performance data for impregnated LSM cathode cells made by impregnation of a) aqueous salt solutions, LSM-YSZ (aq), b) molten salt, LSM-YSZ (molten), and c) nano-particle suspension, LSM-YSZ (nano). Based on

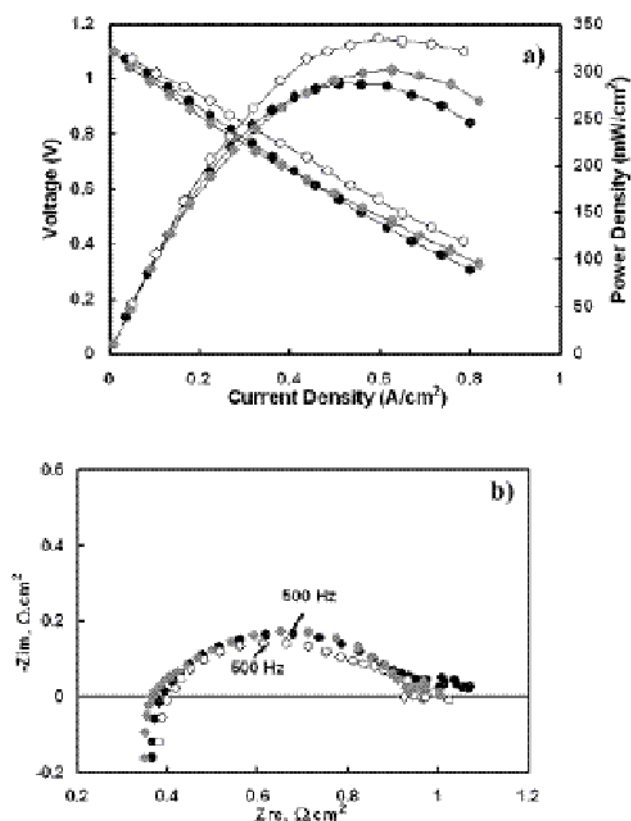


FIGURE 2. Fuel-cell data for cells operating in humidified H_2 (3% H_2O) at 973 K with LSM-YSZ cathodes prepared using different impregnation methods, followed by calcination at 1,323 K: a) V-I Polarization curves; b) Cole-Cole plots of impedance data measured in humidified H_2 (3% H_2O) at 973 K at 300 mA/cm². (●) LSM-YSZ (aq); (●) LSM-YSZ (nano); (○) LSM-YSZ (molten).

previous work, we have estimated that the Co-ceria-YSZ anode in these cells contributes an impedance of approximately $0.2 \Omega \cdot \text{cm}^2$, independent of current density. The resistance associated with the electrolytes in each of the cells is predicted to be above $0.3 \Omega \cdot \text{cm}^2$, in reasonable agreement with the observed high-frequency impedance between 0.35 and $0.40 \Omega \cdot \text{cm}^2$ observed in Figure 2b. Therefore, it is straightforward to extract the performance of the cathodes from these data, namely in the range of 0.4 to $0.5 \Omega \cdot \text{cm}^2$.

B. Stability Studies of LSF-YSZ Electrodes

This work is still ongoing but recent data obtained with a “symmetric” cell appears to be the most reliable information we have on the stability of the LSF-YSZ electrodes. This data is shown in Figure 3. The data shows that the ohmic resistance of the cell does not appear to be changing over a period of 1,300 h. That is very encouraging, since any solid-state reactions at the interface between the electrolyte and the electrode would be expected to form insulating layers that would

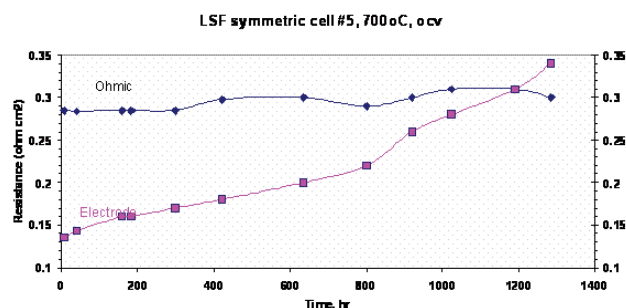


FIGURE 3. Results from a "symmetric" cell, using one of the LSF-YSZ electrodes as a support. One of the LSF-YSZ electrodes is 300 microns thick, while the other is 50 microns. The electrolyte is approximately 70 microns thick. The data in the figure shows the total ohmic and polarization resistances, divided by two to account for the two electrodes.

result in an increased ohmic resistance. However, significant increases have occurred in the polarization losses. While it is possible that these could be due to diffusion through the Ag contact paste, we suggest that something else is causing the increase. We are still attempting to identify the mechanism for this deactivation.

Conclusions and Future Directions

- The cathode properties of LSM-YSZ composites formed by infiltration of porous YSZ with aqueous salt solutions, with LSM nano-particles, and with molten salts are essentially identical. The relatively high mobility of LSM on YSZ, associated with surface interactions between LSM and YSZ, causes the final composite structures to be essentially the same, independent of how the LSM is added.

Infiltration of the molten salt allows for the fewest number of infiltration steps, as few as two steps, while infiltration with nano-particles required as many as 40 steps.

- We have preliminary results on the deactivation of LSF-YSZ electrodes at 973 K. Ohmic losses appear to be stable after 1,300 h. However, we are observing an increase in the polarization losses after this period of time. We are presently working to identify the deactivation mechanism.

Special Recognitions & Awards/Patents Issued

- US Patent # 6,958,196, "Porous Electrode, Solid Oxide Fuel Cell, and Method of Producing the Same", issued October 25, 2005.

FY 2006 Publications/Presentations

- "An Examination of LSM-LSCo Mixtures for Use in SOFC Cathodes", Y. Huang, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, Journal of the Electrochemical Society, 153 (2006) A951-55.
- "SOFC Cathodes Prepared by Infiltration with Various LSM Precursors", Y. Huang, J. M. Vohs, and R. J. Gorte, Electrochemical & Solid-State Letters, 9 (2006) A237-240.

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